

Electrochemical Study of Complexation Behavior of Uridine with some common Metal Ions in Aqueous Media

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ABSTRACT

Polarographic study of complexation of uridine with some transition metal cations Ni(II), Cu(II) and Zn(II) in aqueous solution at ion strength 0.1 M LiClO₄ yield stability constant values, logK₁ and logK₂ at 298K as 2.91, 0.94; 3.03, 0.89 and 2.71, 1.11 respectively. The values follow Irving-William natural order. ΔG, ΔH and ΔS values calculated in the range 293-303 K were found to be negative indicating complex formation in the aqueous media as spontaneous and greater order in the complex molecule.

Keywords: Complexation behavior of Uridine, Aqueous Media.

INTRODUCTION

The importance of metal ion-mediated reaction involving nucleic acid constituents e.g. nucleosides is well recognized and applied¹⁻⁴. Among the nucleosides, pyrimidines possess fewer coordination sites compared to purines, still they are found to exhibit coordinating behaviour⁵. Knowledge on uridine complexes is scarce and least studied like its base, uracil. The metal binding capacity of uridine depends on the pH of the reacting medium. It contains three potential metal ion binding sites viz. O(2), N(3) and O(4). The dissociation of a proton from N(3) occurs

only at a high pH (~ 9.0) leaving the other two as viable alternate sites for metal ion binding at biological pH. Among these two, O(4) is preferred as it possesses high electron density compared to O(2).⁶⁻⁸

The present study comprises polarographic investigation of complexation of uridine with common transition metal ions Ni(II), Cu(II) and Zn(II) in aqueous media in order to have more information regarding interactions. The stability constant values of complex formation were determined by Crow's mean diffusion coefficient method assuming 1:1 complexation.⁹⁻¹⁰ Thermodynamic parameters

e.g. free energy, enthalpy and entropy were also calculated.

EXPERIMENTAL

For the record of polarogram, an ELICO (CL-25D) polarograph with chart recorder (LR-101P) were used. pH were maintained using ELICO pH meter (LI-120) and temperature of the solution were maintained by circulating water from Julabo (F-40HC, Germany) cryostat to double walled H-shaped Kalousek cell with an in-built SCE. The characteristic of capillary used were $m=1.722 \text{ mgs}^{-1}$, $t=5.3\text{sec}$ (open circuit) and $h_{\text{uncorr}} = 70 \text{ cm}$. Hg in aqueous 0.1 N LiClO_4 at zero potential. Uridine used in the investigation was obtained from SRL India. All other reagents were of extra pure (E.Merek) or A.R. grade.

The composition of the test solution were (a) MClO_4 (Ni(II): 0.4 mmol dm^{-3} , Cu(II): 0.3 mmol dm^{-3} and Zn(II): 0.4 mmol dm^{-3}) + LiClO_4 (2.5ml 1.0 mol dm^{-3}) + gelatin (0.5 ml 0.2%) (b) (a) + increasing volume of uridine. The total volume of the solution were made up to 25 ml with water after adjusting pH by adding LiOH and HClO_4 as required. The concentration of supporting electrolyte were maintained constant at 0.1 mol dm^{-3} (LiClO_4). The pH for Ni(II), Cu(II) and Zn(II) solution were kept below this precipitation pH e.g. at 6.0, 5.0 and 6.0 (+0.05) respectively.

Polarograms for each metal ion were recorded at three temperatures. 293, 298 and 303K ($\pm 0.1\text{K}$) for the determination of thermodynamic parameters. Purified IOLAR grade nitrogen was passed through the solution for fifteen minutes before recording polarogram.

RESULTS AND DISCUSSION

Polarographic data for the complexation of uridine with Ni(II), Cu(II) and Zn(II) at 298K are presented in table-1. In all the cases, electroreduction of aqueous metal ion as well as complexed metal ion exhibit a well defined polarographic waves. The limiting current versus \sqrt{h} plots are linear, passing through the origin indicating diffusion controlled nature of the waves. For the case of Ni(II) the wave slopes vary from 70mV to 51mV (298K) for complexed metal ion from the lowest to the highest ligand concentration, showing the irreversible nature with the reduction process tending to become more reversible with increasing ligand concentration. Negative shifts of half-wave potentials have been observed on addition of the ligand. In the case of Cu(II) the wave-slopes for aquo- and complexed metal ions are around 44mV, indicating the reduction process to be quasi-reversible. The usual negative shift of waves occur on complexation. The slopes of the waves for Zn(II) vary from 57mV to 45 mV indicating irreversible nature of the reduction process from the lowest to highest ligand concentration at 298K. No shift in half-wave potential observed for this system.

The pseudo-formation curves (plot of Δi_d Vs. $-\log[L]$) for all the system, on integration at different ligand concentration give the value of $\log F_0'[L]^{11}$. The $\log F_0'[L]$ values were then plotted against $-\log[L]$, the limiting slopes of which yield (N_{max}/K) value. From the knowledge of the N_{max} for each metal ion (assumed to be one), give K value. The K values were then used to calculate the $F_0[L]$ functions, from which other Leden function $F_j[L]$ were obtained by

the plots of $F_j[L]$ Vs. $[L]$. The intercepts on the $F_j[L]$ axes give the formation constants. The stability constant values for all the system were calculated^{9,10,12,13}. All the values at three temperatures are listed in table-2. From the stability constant values at three temperatures 293,298 and 303K, thermodynamic parameters ΔG , ΔH and ΔS for complex formation were calculated and shown in table-2.

The stability constant values for the three system approximately obeyed Irving

and Williams¹⁴ and Mellor and Maley¹⁵ natural order i.e. Ni (II)< Cu(II)>Zn(II). The free energies and enthalpies of formation in each case have large negative values indicative of complex formation to be spontaneous. The negative values of entropy show higher order in the complex molecule. The stability constant values at higher temperature are less than that of at lower temperature confirming the finding that higher temperatures are not favourable for complex formation¹⁶.

TABLE-1

Complexation of uridine with Ni(II), Cu(II) and Zn(II) in aqueous media at ionic strength 0.1 M LiClO₄.

LiClO₄: Ni(II) and Zn(II): 0.4 mmol dm⁻³ Cu(II): 0.3 mmol dm⁻³ Temperature:298K

LiClO₄: 0.1mol dm⁻³

Sl. No.	$[L] \times 10^4$ mol dm ³	$i_d(\text{Ni})$ μA	$E_{1/2}(\text{Ni})$ V	$i_d(\text{Cu})$ μA	$-E_{1/2}(\text{Cu})$ V	$i_d(\text{Zn})$ μA	$-E_{1/2}(\text{Zn})$ V
1	-	2.050	0.97	1.230	+0.050	1.76	1.01
2	0.8	2.000	0.98	-	-	1.75	1.01
3	4	1.975	0.98	1.210	+0.040	1.74	1.01
4	8	1.965	0.99	1.200	+0.040	1.73	1.01
5	16	1.925	0.99	1.180	+0.040	1.71	1.01
6	40	1.875	1.01	1.165	+0.040	1.70	1.01
7	80	1.825	1.01	1.150	+0.040	1.68	1.01
8	200	1.730	1.02	1.140	+0.030	1.64	1.01

TABLE-2

Stability Constants and Thermodynamic parameters for M(II)-Uridine complexes in aqueous medium at ionic strength 0.1 M LiClO₄.

	Temperature K	logK ₁	logK ₂	$\frac{-\Delta G}{\text{kJ mol}^{-1}}$	$\frac{-\Delta H}{\text{kJ mol}^{-1}}$	$\frac{-\Delta S}{\text{J mol}^{-1}\text{K}^{-1}}$
Ni(II)	293	2.96	1.12	16.61	26.11	-32.33
	298	2.91	0.94	16.60		
	303	2.81	0.98	16.30		
Cu(II)	293	3.13	0.66	17.56	38.29	-70.69
	298	3.03	0.89	17.29		
	303	2.90	0.84	16.83		
Zn(I)	293	2.81	1.07	15.76	34.47	-13.85
	298	2.71	1.11	15.46		
	303	2.60	1.24	15.08		

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